

Phase Relations in the SrO–IrO₂–Ir System in Air

C. L. McDaniel and S. J. Schneider

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

(February 3, 1971)

The equilibrium phase relations for the SrO–IrO₂–Ir system were determined in an air environment at atmospheric pressure. A ternary equilibrium phase diagram was constructed indicating selected oxygen reaction lines and tie lines. A binary representation is given for the ternary system in air. Of the nine phases detected in this study, three are stable and six are probably metastable under atmospheric conditions. The stable compounds, 4SrO · IrO₂, 2SrO · IrO₂, and SrO · IrO₂ dissociate at 1540, 1445, and 1205 °C, respectively. The metastable phases include low-4SrO · IrO₂, 2SrO · 3IrO₂, x SrO · IrO₂ ($x > 2$), y SrO · IrO₂ ($4 > y > 2$), z SrO · IrO₂ ($2 > z > 1$), and 3SrO · 2IrO₂. The specific composition of the metastable phases could not be ascertained with certainty. The x-ray patterns of all phases detected in this study were indexed with the exception of that of the z SrO · IrO₂ ($2 > z > 1$) compound. A summary of x-ray data is given for all known phases occurring in the system.

Key words: Dissociation; equilibrium; phase relations; SrO:IrO₂ compounds; SrO–IrO₂–Ir system.

1. Introduction

The present study is part of a program [1, 2, 3]¹ to obtain a better understanding of the behavior of various Pt-group metals and metal oxides when heated together in an oxidizing environment. Considering the fact that several of these metals are used as secondary standards on the International Practical Temperature Scale (ITS 1968)² [4] as well as for container materials for high temperature applications, knowledge of the phase relations between these metals and other materials becomes important. This work presents the results of an investigation of the equilibrium relationships between the condensed phases in the system SrO–IrO₂–Ir in air.

Strontium oxide (SrO) has a cubic, sodium chloride-type structure with $a = 5.1602$ Å [5]. The melting point of SrO has been reported to be 2424 °C [6].

Iridium (Ir) has a face-centered cubic, copper-type structure with $a = 3.8394$ Å [7]. Its freezing point, 2447 °C, is listed as a secondary reference point on the ITS (1968).

Iridium has a strong tendency to form iridium dioxide (IrO₂) when heated in air at moderate temperatures. The unit cell dimensions of IrO₂ are reported as (tetragonal) $a = 4.4983$ Å and $c = 3.1544$ Å [8]. However, above 1021 °C [2] Ir metal is the only solid phase that exists in equilibrium with air.

Even though Ir oxidizes to IrO₂ when heated in air, complete oxidation of the entire sample is often difficult to obtain. By utilizing IrO₂ rather than Ir as starting material, an approach to equilibrium could be achieved

more readily. The study will still reflect, however, the behavior of the metal in air.

2. Experimental Procedure

Specimens were prepared from 0.4 g batches of various combinations of strontium carbonate (SrCO₃) and IrO₂, each having a purity of at least 99.8 percent. Calculated amounts of these end members, corrected for ignition loss, were weighed to the nearest milligram. Each batch was thoroughly hand mixed and calcined in a muffle furnace at a minimum temperature of 800 °C or heated directly at the temperature of interest. Specimen containers employed in this study were open or sealed gold tubes, open or sealed platinum tubes, and open fused silica tubes. Portions of each calcined batch were refired in a platinum alloy wire-wound quench furnace at various temperatures for different periods of time. The specimens were quenched in air, ice water, or liquid nitrogen. Temperatures in the quench furnace were measured with a Pt versus 90 percent Pt-10 percent Rh calibrated thermocouple. All reported temperatures pertaining to quench furnace data are considered accurate to within ± 5 °C. The precision of the measurements was estimated to be ± 2 °C.

Equilibrium was assumed to have been achieved when the x-ray pattern showed no change after successive heat treatments of the specimen or when the data were consistent with the results from a previous set of experiments. An attempt was made on various compositions to obtain equilibrium by increasing the oxygen pressure of the environment exposed to the specimen. The specimen was placed in an open gold tube and heated at moderate temperatures to decom-

¹Figures in brackets indicate the literature references at the end of this paper.

²This scale (ITS 1968) applies to all temperatures listed in this paper.

pose the SrCO_3 . The open gold tube containing the specimen was then placed into a larger platinum tube containing a calculated amount of finely divided platinum dioxide (PtO_2). The platinum tube was then sealed by welding and heat treated at a given temperature. As the temperature was raised the PtO_2 decomposed and increased the oxygen pressure, calculated to be approximately 30 atm ($3.03975 \times 10^6 \text{ N/m}^2$). The container materials did not appear to influence or react with the various oxide samples. All phases detected in this study were formed in air using gold as well as Pt for container materials.

All specimens were examined by x-ray diffraction

at room temperature using a high-angle-recording Geiger counter diffractometer and Ni-filtered Cu radiation. The scanning rate was $\frac{1}{4}^\circ 2\theta/\text{min}$. Unit cell dimensions were refined by a least-squares computer program and are estimated to be accurate to at least 2 in the last decimal place listed.

3. Results and Discussion

3.1. Phase Diagram

The equilibrium phase diagram for the $\text{SrO-IrO}_2\text{-Ir}$ system in air is given in figure 1. The diagram was con-

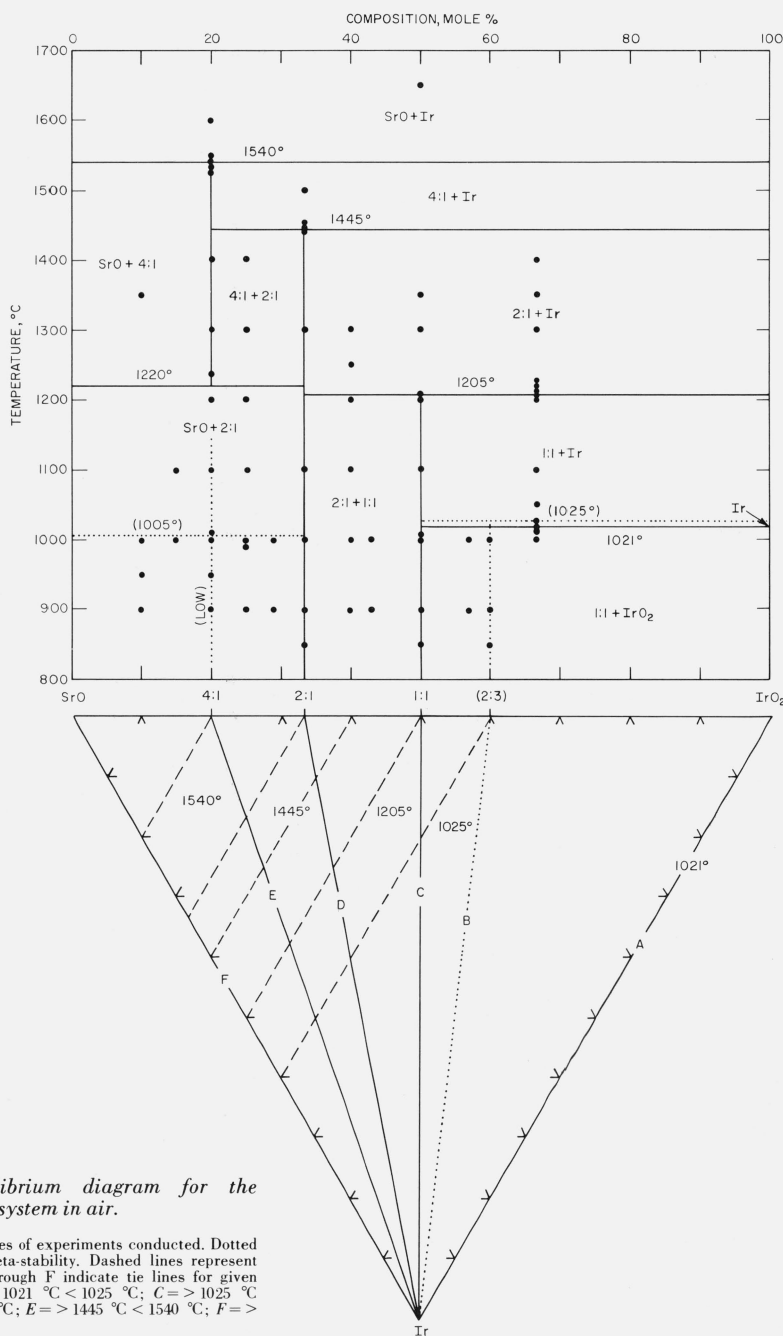


FIGURE 1. Phase equilibrium diagram for the $\text{SrO-IrO}_2\text{-Ir}$ system in air.

●—compositions and temperatures of experiments conducted. Dotted lines and parentheses indicate meta-stability. Dashed lines represent oxygen reaction lines. Lines A through F indicate tie lines for given temperatures, $A = 1021^\circ \text{C}$, $B = > 1021^\circ \text{C} < 1025^\circ \text{C}$; $C = > 1025^\circ \text{C} < 1205^\circ \text{C}$; $D = > 1205^\circ \text{C} < 1445^\circ \text{C}$; $E = > 1445^\circ \text{C} < 1540^\circ \text{C}$; $F = > 1540^\circ \text{C}$.

structured from the data listed in table 1. The solid circles illustrate the compositions and temperatures of the experiments conducted. The dotted lines and parentheses indicate metastability. In the ternary plot the dashed lines represent oxygen reaction lines. Lines A through F indicate tie lines. The three phase triangular areas with listed temperatures represent invariant situations in which three condensed phases co-exist in equilibrium at those specified temperatures. The oxygen reaction lines connect compositions on the SrO-IrO₂ join and the final compositions attained upon dissociation of the oxide mixtures. The dissocia-

tion products are Ir and one of the following: SrO · IrO₂, 2SrO · IrO₂, 4SrO · IrO₂, or SrO. It should be emphasized that these dissociation products are the condensed phases of the system and are always in equilibrium with oxygen. The tie lines (A-F) represent joins for a given temperature or series of temperatures for any series of intersecting oxygen reaction lines.

Consider for instance a 50:50 mole percent mixture on the SrO-IrO₂ join. At temperatures below 1205 °C, the mixture contains one solid phase, the 1:1 compound. As this phase is heated to higher temperatures, oxygen loss occurs, producing a situation in which two

TABLE 1. *Experimental data for compositions in the SrO-IrO₂-Ir system*

Composition		Heat treatment ^a		X-ray diffraction analyses ^g	Remarks
SrO	IrO ₂	Previous ^b	Final		
Mol%	Mol%	°C-h	°C-h		
90	10		700-68 ^e 900-3	SrCO ₃ + xSrO · IrO ₂ (x > 2) SrCO ₃ + IrO ₂	Nonequilibrium. No reaction; nonequilibrium.
			900-3 ^e 900-18	SrCO ₃ + xSrO · IrO ₂ (x > 2) SrCO ₃ + IrO ₂	Nonequilibrium. No reaction; nonequilibrium.
			^f 950-272 1000-2	4SrO · IrO ₂ + xSrO · IrO ₂ (x > 2) SrO + xSrO · IrO ₂ (x > 2) + 4SrO · IrO ₂ + low - 4SrO · IrO ₂	Nonequilibrium. Nonequilibrium. Nonequilibrium.
		^f 900-3 1350-2	^d 1000-4 ^f 1000-96 ^f 1000-72	low - 4SrO · IrO ₂ + SrCO ₃ 4SrO · IrO ₂ + SrO 4SrO · IrO ₂ + SrO + xSrO · IrO ₂ (x > 2) + low - 4SrO · IrO ₂	Nonequilibrium.
			^f 1000-168 1350-2	4SrO · IrO ₂ + SrO 4SrO · IrO ₂ + SrO	Nonequilibrium.
85	15		800-18	SrCO ₃ + ySrO · IrO ₂ (4 > y > 2) + low - 4SrO · IrO ₂	Nonequilibrium.
		800-18 800-18, 1000-21	1000-21 1100-66	low - 4SrO · IrO ₂ + SrO 4SrO · IrO ₂ + SrO	Nonequilibrium.
80	20	^f 800-67, ^f 1000-20, ^f 1000-20, 1400-3	800-18 ^f 800-67 ^d 900-66	4SrO · IrO ₂ low - 4SrO · IrO ₂ + SrCO ₃ + xSrO · IrO ₂ (x > 2) low - 4SrO · IrO ₂ + SrCO ₃ + IrO ₂	Nonequilibrium. Nonequilibrium; trace amounts of SrCO ₃ and IrO ₂ .
		^f 800-67, ^f 1000-20, ^f 1000-20, 1400-3	^f 950-192 ^f 1000-0.5	4SrO · IrO ₂ low - 4SrO · IrO ₂ + xSrO · IrO ₂ (x > 2)	Nonequilibrium.
		900-2 ^f 900-2 1400-3	^e 1000-1 ^d 1000-2 1000-18	ySrO · IrO ₂ (4 > y > 2) + low - 4SrO · IrO ₂ + SrCO ₃ low - 4SrO · IrO ₂ + ySrO · IrO ₂ (4 > y > 2) + SrCO ₃ 4SrO · IrO ₂ + 2SrO · IrO ₂ + xSrO · IrO ₂ (x > 2)	Nonequilibrium. Nonequilibrium. Nonequilibrium. Quenched in liquid nitro- gen; nonequilibrium.
		1400-3	^e 1000-18	4SrO · IrO ₂ + 2SrO · IrO ₂	Quenched in liquid nitro- gen; nonequilibrium.
		900-2 1300-2 ^f 800-67 ^f 800-67, ^f 1000-20 1400-3 1400-3 1400-3	^e 1000-19 1000-19 ^f 1000-20 ^f 1000-20 1000-21 ^c 1000-72 1000-72	2SrO · IrO ₂ + low - 4SrO · IrO ₂ + SrCO ₃ 4SrO · IrO ₂ + 2SrO · IrO ₂ + xSrO · IrO ₂ (x > 2) low - 4SrO · IrO ₂ + 4SrO · IrO ₂ + xSrO · IrO ₂ (x > 2) 4SrO · IrO ₂ + low - 4SrO · IrO ₂ + xSrO · IrO ₂ (x > 2) 4SrO · IrO ₂ + 2SrO · IrO ₂ + xSrO · IrO ₂ (x > 2) 4SrO · IrO ₂ + 2SrO · IrO ₂ + xSrO · IrO ₂ (x > 2) 2SrO · IrO ₂ + unidentified phase	Nonequilibrium. Nonequilibrium. Nonequilibrium. Nonequilibrium. Nonequilibrium. Nonequilibrium. Quenched in ice water; unidentified phase prob- ably a hydrate.
		1400-3	^f 1000-72	2SrO · IrO ₂ + unidentified phase	Quenched in ice water; unidentified phase prob- ably a hydrate.

Footnotes at end of table.

TABLE 1. *Experimental data for compositions in the SrO-IrO₂-Ir system—Continued*

Composition		Heat treatment ^a		X-ray diffraction analyses ^g	Remarks
SrO	IrO ₂	Previous ^h	Final		
<i>Mol%</i>	<i>Mol%</i>	<i>°C-h</i>	<i>°C-h</i>		
75	25	1400-3	1000-66	4SrO·IrO ₂ + 2SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$)	Nonequilibrium. Quenched in ice water; nonequilibrium. Nonequilibrium.
		1400-3	^b 1000-96	4SrO·IrO ₂ + 2SrO·IrO ₂	
		^f 800-67, ^f 1000-20, ^f 1000-20	1010-20	4SrO·IrO ₂ + 2SrO·IrO ₂	
		1400-3	^e 1100-18	4SrO·IrO ₂ + 2SrO·IrO ₂	Nonequilibrium.
		^f 800-67, ^f 1000-20, ^f 1000-20, 1400-3	1100-66	4SrO·IrO ₂ + 2SrO·IrO ₂	Nonequilibrium. Nonequilibrium.
		1400-3	^e 1200-22	4SrO·IrO ₂ + 2SrO·IrO ₂	
		^f 800-67, ^f 1000-20, ^f 1000-20, 1400-3	1200-63	4SrO·IrO ₂ + 2SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$)	Nonequilibrium.
		1400-3	^e 1235-17	4SrO·IrO ₂	
		1400-0.5	^e 1300-65	4SrO·IrO ₂	Quenched in liquid nitro- gen. Quenched in ice water; unidentified phase prob- ably a hydrate.
		1400-2	1400-0.5	4SrO·IrO ₂	
		1400-2	1400-0.5	unidentified phase + 2SrO·IrO ₂	
			1400-2	4SrO·IrO ₂	
		^f 800-67, ^f 1000-20, ^f 1000-20	1400-3	4SrO·IrO ₂	
		1400-2, 1600-2	1400-18	4SrO·IrO ₂	
		1400-2	1540-2	4SrO·IrO ₂ + SrO	
		1400-2	1550-2	4SrO·IrO ₂ + SrO	
		1400-2	1525-2	4SrO·IrO ₂	
		1400-2	1535-2	4SrO·IrO ₂	
		1400-2	1600-2	4SrO·IrO ₂ + SrO	
		^f 900-3	^d 800-17	low - 4SrO·IrO ₂ + 2SrO·3IrO ₂ + ySrO·IrO ₂ ($4 > y > 2$)	
			^f 800-20	low - 4SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$) + SrCO ₃ + ySrO·IrO ₂ ($4 > y > 2$)	
			900-2	low - 4SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$)	
			900-17	xSrO·IrO ₂ ($x > 2$) + low - 4SrO·IrO ₂	
		^f 900-3	^d 900-17	low - 4SrO·IrO ₂ + 2SrO·IrO ₂ + ySrO· IrO ₂ ($4 > y > 2$)	
		^f 800-20, ^f 1000-20, ^f 1000-21	900-65	2SrO·IrO ₂ + low - 4SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$)	Nonequilibrium. Nonequilibrium.
		^f 900-2	^d 900-66	low - 4SrO·IrO ₂ + 2SrO·IrO ₂ + ySrO· IrO ₂ ($4 > y > 2$)	
		900-2	^e 900-71	low - 4SrO·IrO ₂ + 2SrO·IrO ₂	Nonequilibrium.
		^f 800-20, ^f 1000-20, ^f 1000-21, 1300-2	990-18	4SrO·IrO ₂ + 2SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$)	Nonequilibrium. Nonequilibrium.
		^f 900-2	^d 1000-2	xSrO·IrO ₂ ($x > 2$) + 4SrO·IrO ₂ + low - 4SrO·IrO ₂ ySrO·IrO ₂ ($4 > y > 2$) + low - 4SrO·IrO ₂	
		1300-2	1000-18	2SrO·IrO ₂ + 4SrO·IrO ₂	Quenched in ice water; unidentified phase prob- ably a hydrate.
		1300-2	1000-19	2SrO·IrO ₂ + unidentified phase	
		900-2	^e 1000-19	2SrO·IrO ₂ + low - 4SrO·IrO ₂	Nonequilibrium. Nonequilibrium.
		^f 800-20	^f 1000-20	low - 4SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$) + 2SrO·IrO ₂	
		^f 800-20, ^f 1000-20	^f 1000-20	low - 4SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$) + 2SrO·IrO ₂	Nonequilibrium. Nonequilibrium.
		^f 800-20, ^f 1000-20, ^f 1000-20, 1300-2	1000-96	2SrO·IrO ₂ + 4SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$)	
		1000-20	1100-68	2SrO·IrO ₂ + xSrO·IrO ₂ ($x > 2$) + 4SrO·IrO ₂	Nonequilibrium. Nonequilibrium.
		^f 800-20, ^f 1000-20, ^f 1000-20	1100-288	2SrO·IrO ₂ + 4SrO·IrO ₂	
		^f 800-20, ^f 1000-20, ^f 1000-20	^e 1100-288	2SrO·IrO ₂ + 4SrO·IrO ₂ + low - 4SrO·IrO ₂	Nonequilibrium.
		1000-20	1200-2	2SrO·IrO ₂ + 4SrO·IrO ₂	
		1000-20	1300-2	2SrO·IrO ₂ + 4SrO·IrO ₂	
		^f 800-20, ^f 1000-20, ^f 1000-20, 1300-2,	1400-2	2SrO·IrO ₂ + 4SrO·IrO ₂	
		1300-2, 1000-19			1000-19 Heat quenched in ice water.
71	29	^f 900-2	^d 1000-2	2SrO·IrO ₂ + low - 4SrO·IrO ₂	Nonequilibrium.

Footnotes at end of table.

TABLE 1. *Experimental data for compositions in the SrO-IrO₂-Ir system—Continued*

Composition		Heat treatment ^a		X-ray diffraction analyses ^g	Remarks
SrO	IrO ₂	Previous ^b	Final		
<i>Mol%</i> 66.6	<i>Mol%</i> 33.3	^{°C-h}	^{°C-h}		
		<i>f</i> 800–20	<i>f</i> 800–67	2SrO·3IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2) + low – 4SrO	Nonequilibrium.
				·IrO ₂ + <i>y</i> SrO·IrO ₂ (<i>4</i> > <i>y</i> > 2)	Nonequilibrium.
				2SrO·3IrO ₂ + <i>y</i> SrO·IrO ₂ (<i>4</i> > <i>y</i> > 2) + low – 4SrO	Nonequilibrium.
				·IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2)	Nonequilibrium.
				2SrO·3IrO ₂ + <i>y</i> SrO·IrO ₂ (<i>4</i> > <i>y</i> > 2) + low – 4SrO	Nonequilibrium.
				·IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2)	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 800–19	<i>f</i> 850–20	2SrO·IrO ₂ + low – 4SrO·IrO ₂ + 2SrO·3IrO ₂	Nonequilibrium.
		<i>f</i> 900–2	<i>d</i> 900–17	2SrO·IrO ₂ + 2SrO·3IrO ₂	Nonequilibrium.
		<i>f</i> 900–2	<i>d</i> 1000–2	2SrO·IrO ₂ + 2SrO·3IrO ₂	Nonequilibrium.
		<i>f</i> 800–67	<i>f</i> 1000–20	2SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800–67, <i>f</i> 1000–20	<i>f</i> 1000–20	2SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20, 1500–2	1000–22	2SrO·IrO ₂ + 4SrO·IrO ₂ + Ir	Nonequilibrium.
			1100–0.5	2SrO·IrO ₂	
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20	1100–20	2SrO·IrO ₂	
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20	1300–63	2SrO·IrO ₂	
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20	1440–2	2SrO·IrO ₂	
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20	1445–2	2SrO·IrO ₂ + 4SrO·IrO ₂	
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20	1450–2	2SrO·IrO ₂ + 4SrO·IrO ₂	
		<i>f</i> 800–67, <i>f</i> 1000–20,			
		<i>f</i> 1000–20	1500–2	4SrO·IrO ₂ + 2SrO·IrO ₂ + Ir	Nonequilibrium.
60	40	<i>f</i> 900–3	<i>d</i> 800–17	2SrO·3IrO ₂ + low – 4SrO·IrO ₂	Nonequilibrium.
			<i>f</i> 800–20	2SrO·3IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2) + low – 4SrO	Nonequilibrium.
				·IrO ₂ + <i>y</i> SrO·IrO ₂ (<i>4</i> > <i>y</i> > 2)	Nonequilibrium.
			<i>f</i> 800–408	2SrO·3IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2) + <i>y</i> SrO	Nonequilibrium.
				·IrO ₂ (<i>4</i> > <i>y</i> > 2)	Nonequilibrium.
		<i>f</i> 900–3	<i>d</i> 900–17	2SrO·3IrO ₂ + 3SrO·2IrO ₂ + low – 4SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 1000–20,			
		<i>f</i> 1000–21	900–65	3SrO·2IrO ₂ + SrO·IrO ₂ + <i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1)	Nonequilibrium.
		<i>f</i> 900–2	<i>d</i> 900–66	2SrO·3IrO ₂ + 2SrO·IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2)	Nonequilibrium.
			<i>f</i> 1000–2	<i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1) + SrO·IrO ₂	Nonequilibrium.
		1300–2	1000–18	2SrO·IrO ₂ + SrO·IrO ₂	
		<i>f</i> 800–20	<i>f</i> 1000–20	3SrO·2IrO ₂ + SrO·IrO ₂ + <i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1)	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 1000–20	<i>f</i> 1000–21	3SrO·2IrO ₂ + SrO·IrO ₂ + <i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1)	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 1000–20,			
		<i>f</i> 1000–21	1100–68	3SrO·2IrO ₂ + SrO·IrO ₂ + <i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1)	Nonequilibrium.
				+ 2SrO·IrO ₂	
		<i>f</i> 800–20, <i>f</i> 1000–20,			
		<i>f</i> 1000–21	1100–288	3SrO·2IrO ₂ + 2SrO·IrO ₂ + <i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1)	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 1000–20,			
		<i>f</i> 1000–21	<i>e</i> 1100–288	3SrO·2IrO ₂ + 2SrO·IrO ₂ + SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 1000–20,			
		<i>f</i> 1000–21	1200–2	3SrO·2IrO ₂ + <i>z</i> SrO·IrO ₂ (<i>2</i> > <i>z</i> > 1) + SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800–20, <i>f</i> 1000–20,			
		<i>f</i> 1000–21	1250–42	2SrO·IrO ₂ + Ir	
			1300–2	2SrO·IrO ₂ + Ir	
57	43		<i>f</i> 800–408	2SrO·3IrO ₂ + <i>x</i> SrO·IrO ₂ (<i>x</i> > 2) + <i>y</i> SrO	Nonequilibrium.
				·IrO ₂ (<i>4</i> > <i>y</i> > 2)	
			900–3	2SrO·3IrO ₂ + 2SrO·IrO ₂ + 3SrO·2IrO ₂ + <i>z</i> SrO	Nonequilibrium.
				·IrO ₂ (<i>2</i> > <i>z</i> > 1) + SrO·IrO ₂	
		<i>f</i> 900–2	<i>d</i> 900–66	2SrO·3IrO ₂ + 2SrO·IrO ₂	Nonequilibrium.
		900–3	<i>e</i> 1000–19	SrO·IrO ₂ + 3SrO·2IrO ₂	Nonequilibrium.
50	50		750–17	2SrO·3IrO ₂ + SrO·IrO ₂	Nonequilibrium.
			<i>f</i> 800–19	2SrO·3IrO ₂ + SrO·IrO ₂	Nonequilibrium.
			<i>f</i> 800–67	2SrO·3IrO ₂ + SrO·IrO ₂	Nonequilibrium.
			<i>f</i> 850–20	2SrO·3IrO ₂ + SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 900–2	<i>d</i> 900–17	2SrO·3IrO ₂ + <i>y</i> SrO·IrO ₂ (<i>4</i> > <i>y</i> > 2)	Nonequilibrium.
				+ SrO·IrO ₂	
		<i>f</i> 900–2	<i>d</i> 1000–2	SrO·IrO ₂ + 2SrO·3IrO ₂	Nonequilibrium.

Footnotes at end of table.

TABLE 1. *Experimental data for compositions in the SrO-IrO₂-Ir system—Continued*

Composition		Heat treatment ^a		X-ray diffraction analyses ^g	Remarks
SrO	IrO ₂	Previous ^b	Final		
<i>Mol%</i>	<i>Mol%</i>	<i>°C-h</i>	<i>°C-h</i>		
		<i>f</i> 800-67	<i>f</i> 1000-20	SrO·IrO ₂ + 2SrO·3IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20	<i>f</i> 1000-20	SrO·IrO ₂	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	<i>f</i> 1000-288	SrO·IrO ₂	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20, 1350-2	1005-17	SrO·IrO ₂	SrO·IrO ₂ reformed from dissociation products.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1100-20	SrO·IrO ₂	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1100-288	SrO·IrO ₂	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	<i>e</i> 1100-288	SrO·IrO ₂	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1200-2	SrO·IrO ₂	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1205-2	SrO·IrO ₂ + 2SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	<i>c</i> 1300-2	2SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20			
		<i>f</i> 1000-20	1300-18	2SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1300-63	2SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1350-2	2SrO·IrO ₂ + Ir	
		1000-18	1650-4	Ir + SrO + SrCO ₃	Nonequilibrium; SrCO ₃ formed on cooling.
47	53		800-18	2SrO·3IrO ₂ + SrO·IrO ₂	Nonequilibrium.
43	57	<i>f</i> 900-2	<i>f</i> 1000-2	2SrO·3IrO ₂ + SrO·IrO ₂	Nonequilibrium.
			<i>f</i> 1000-168	SrO·IrO ₂ + IrO ₂	
40	60		700-18	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		700-18	700-18	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		700-18, 700-18	700-19	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		700-18, 700-18,			
		700-19	700-66	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium; trace amount of IrO ₂ .
		700-18, 700-18,			
		700-19, 700-66	700-456	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium; trace amount of IrO ₂ .
			<i>f</i> 800-20	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
			850-17	SrO·IrO ₂ + 2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 900-2	<i>d</i> 900-17	2SrO·3IrO ₂ + IrO ₂ + SrO·IrO ₂	Nonequilibrium.
			<i>e</i> 900-19	2SrO·3IrO ₂ + IrO ₂ + SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800-20	<i>f</i> 1000-20	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 800-20, <i>f</i> 1000-20	<i>f</i> 1000-21	2SrO·3IrO ₂ + IrO ₂ + SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800-20, <i>f</i> 1000-20,			
		<i>f</i> 1000-21	<i>e</i> 1000-312	2SrO·3IrO ₂ + IrO ₂ + SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800-20, <i>f</i> 1000-20,			
		<i>f</i> 1000-21	1000-408	SrO·IrO ₂ + IrO ₂	
33.3	66.6		<i>f</i> 800-67	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 800-67	<i>f</i> 1000-20	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20	<i>f</i> 1000-20	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1015-2	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1020-2	2SrO·3IrO ₂ + IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1025-2	2SrO·3IrO ₂ + SrO·IrO ₂ + Ir + IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1050-2	SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			

Footnotes at end of table.

TABLE 1. *Experimental data for compositions in the SrO-IrO₂-Ir system—Continued*

Composition		Heat treatment ^a		X-ray diffraction analyses ^g	Remarks
SrO	IrO ₂	Previous ^b	Final		
<i>Mol%</i>	<i>Mol%</i>	<i>°C-h</i>	<i>°C-h</i>		
		<i>f</i> 1000-20	1100-20	SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1200-2	SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1205-2	3SrO·2IrO ₂ + Ir	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1210-2	3SrO·2IrO ₂ + Ir	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1215-2	3SrO·2IrO ₂ + Ir	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1225-2	3SrO·2IrO ₂ + Ir + 2SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1300-2	3SrO·2IrO ₂ + Ir	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1300-18	3SrO·2IrO ₂ + 2SrO·IrO ₂	Nonequilibrium.
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1350-2	2SrO·IrO ₂ + Ir	
		<i>f</i> 800-67, <i>f</i> 1000-20,			
		<i>f</i> 1000-20	1400-2	2SrO·IrO ₂ + Ir	

^a All specimens were heat treated in open platinum tubes and air quenched unless otherwise indicated. All temperatures listed applies to (IPTS 1968).

^b Sealed gold tube container; quenched in ice water.

^c Open fused silica tube container; air quenched.

^d Specimen was placed in an open gold tube, which was placed into a larger platinum tube containing a calculated amount of PtO₂. The platinum tube was then sealed. Oxygen pressure calculated to be approximately 30 atm (3.03975×10^6 N/m²).

^e Sealed platinum tube container; quenched in ice water.

^f Open gold tube container; air quenched.

^g Phases identified are given in order of the relative amount present at room temperature; of those intermediate phases listed the following are believed to be metastable in air at atmospheric pressure, low 4SrO·IrO₂, *x*SrO·IrO₂ (*x* > 2), *y*SrO·IrO₂ (*4* > *y* > 2), *z*SrO·IrO₂ (*2* > *z* > 1), 3SrO·2IrO₂, and 2SrO·3IrO₂.

^h No entry under "previous" column indicates the specimen received no prior heat treatment.

or three solid phases are in equilibrium for a given temperature. By following the oxygen reaction lines in figure 1, the specific phases in equilibrium can be established. For example, at 1205 °C, three phases (2:1, 1:1, Ir) exist in equilibrium and for temperatures greater than 1205 °C and less than 1445 °C, two phases (2:1, Ir) exist as illustrated by tie line D. The behavior of any arbitrary mixture, e.g., 60:40, can be established in a similar manner by following the appropriate oxygen reaction line.

The binary-type phase diagram given in the top portion of figure 1 is a projection of certain elements of the three dimensional ternary system SrO-IrO₂-Ir on a two dimensional plane figure. The diagram in effect represents a composite of the SrO-Ir and SrO-IrO₂ systems. As the temperature is increased, the compositions of the solid phases change by an apparent oxygen loss to those indicated by the SrO-Ir join. By illustrating a dissociation as a type of phase transition or decomposition in which the vapor phase is ignored, a simple binary representation of the phase relations of the ternary system can be given. This method of illustration has been employed by a number of investigators [9, 10]. The diagram can be interpreted as a binary system and the application of the lever law is valid.

It was found in earlier work that IrO₂ dissociates to Ir metal and oxygen at 1021 °C in air at atmospheric pressure [2]. This dissociation is a reversible process.

Other investigators [11, 12] have reported that IrO₂ combines with oxygen to form IrO₃, which is stable only in the gaseous state. Stoichiometric IrO₂ apparently is the only condensed Ir-oxide phase stable in an air environment at atmospheric pressure. Furthermore, this study did not detect any evidence for solid solutions in the system which would indicate oxygen-deficient oxides or oxygen-rich metal phases.

3.2. Compounds

a. Stable Phases

Randall and Katz [13] previously reported that 4SrO·PtO₂ and 4SrO·IrO₂ (4:1) have the same type structure (K₄CdCl₆ type) but give no specific x-ray data on the Ir compound. Table 2 gives the x-ray diffraction powder pattern of the 4SrO·IrO₂ compound indexed on the basis of a hexagonal (rhombohedral) cell with *a* = 9.736 Å and *c* = 11.886 Å.

The 4:1 compound is stable only between 1220 and 1540 °C. At the higher temperature, the phase dissociates to SrO, Ir, and oxygen, while at temperatures below the minimum, 1220 °C, the phase slowly decomposes during prolonged heat treatments. The decomposition products generally are the 2SrO·IrO₂ (2:1) compound and another metastable phase *x*SrO·IrO₂ (*x* > 2). The stability of the 4:1 compound was established by heating a specimen first above and

then below the dissociation temperature. The 4:1 compound always reformed from the dissociation products.

TABLE 2. *X-ray diffraction powder data for the 4SrO · IrO₂ and low 4SrO · IrO₂ compounds (CuK α Radiation)^a*

4SrO · IrO ₂ ^b				Low 4SrO · IrO ₂ ^c			
<i>d</i> (Å)				<i>d</i> (Å)			
<i>hkl</i>	obs	calc	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	obs	calc	<i>I</i> / <i>I</i> ₀
110 } 4.87	4.87	}	74	002	9.43	9.39	4
012 } 4.86	4.86			100	8.56	8.54	11
202 } 3.440	3.439	}	3	102	6.316	6.318	15
113 } 3.075	3.073			111	4.769	4.768	15
300 } 2.812	2.811	}	100	004	4.699	4.697	10
122 } 2.809	2.809			112	4.367	4.365	16
024 } 2.430	2.429	}	54	200	4.269	4.269	6
131 } 2.295	2.295			113	3.872	3.873	11
214 } 2.175	2.173	}	50	114	3.400	3.400	3
223 } 2.075	2.074			210	3.228	3.227	7
042 } 1.987	1.987	}	5	212	3.053	3.052	4
006 } 1.981	1.981			115	2.990	2.988	82
125 } 1.905	1.906	}	4	106	2.940	2.940	5
134 } 1.837	1.838			300	2.845	2.846	100
116 } 1.835	1.835	}	24	214	2.660	2.660	4
404 } 1.719	1.719			116	2.642	2.643	26
051 } 1.668	1.670	}	9	206	2.523	2.525	7
413 } 1.669	1.669			221	2.443	2.444	7
330 } 1.623	1.623	}	35	304	2.434	2.434	9
502 } 1.621	1.622			310	2.369	2.368	3
324 } 1.621	1.621	}	3	311	2.350	2.350	4
241 } 1.5791	1.5794			008	2.348	2.348	
422 } 1.5389	1.5391	}	7	312	2.296	2.296	5
226 } 1.5362	1.5365			216	2.246	2.247	19
511 } 1.5019	1.5023	}	3	314	2.114	2.115	3
333 } 1.5017	1.5017			306	2.106	2.106	3
054 } 1.4667	1.4667	}	12	402	2.082	2.082	6
018 } 1.4630	1.4633			225	2.061	2.061	38
600 } 1.4054	1.4053	}	17	320	1.960	1.959	4
208 } 1.4017	1.4013			226	1.936	1.937	13
137 } 1.3739	1.3741	}	3	0, 0, 10	1.878	1.879	6
520 } 1.3498	1.3502			411	1.854	1.854	3
34 } 1.3500	1.3500	}	14	308	1.811	1.811	6
416 } 1.3481	1.3482			413	1.786	1.786	2
128 } 1.3470	1.3467	}	17	219	1.753	1.753	6
425 } 1.3235	1.3236			415	1.669	1.669	22
161 } 1.2783	1.2784	}	7	326	1.661	1.661	8
523 } 1.2780	1.2780			330	1.643	1.643	16
119 } 1.2746	1.2746	}	6	421	1.608	1.608	4
612 } 1.2566	1.2568			416	1.601	1.601	11
318 } 1.2538	1.2541	}	5	3, 0, 10	1.567	1.568	13
048 } 1.2145	1.2145			334	1.550	1.551	4
532 } 1.1805	1.1806	}	4	510	1.533	1.534	3
238 } 1.1782	1.1783			511	1.529	1.529	3
229 } 1.1610	1.1608	}	4	2, 2, 10	1.493	1.494	5
615 } 1.1310	1.1310			513	1.490	1.490	5
704 } 1.1164	1.1163	}	13	600	1.4231	1.4231	10
508 } 1.1147	1.1148			3, 0, 12	1.3715	1.3717	5
624 } 1.0881	1.0881	}	5	338	1.3463	1.3464	3
541 } 1.0753	1.0752			509	1.3217	1.3217	4
419 } 1.0730	1.0729	}	3	2, 2, 12	1.3218	1.3215	
630 } 1.0625	1.0623			525	1.2847	1.2849	5
452 } 1.0622	1.0622	}	6	0, 0, 15	1.2527	1.2524	4

TABLE 2. *X-ray diffraction powder data for the 4SrO · IrO₂ and low 4SrO · IrO₂ compounds (CuK α Radiation)^a—Continued*

4SrO · IrO ₂ ^b				Low 4SrO · IrO ₂ ^c			
<i>d</i> (Å)				<i>d</i> (Å)			
<i>hkl</i>	obs	calc	<i>I</i> / <i>I</i> ₀	<i>hkl</i>	obs	calc	<i>I</i> / <i>I</i> ₀
158	1.0605	1.0606	5	519	1.2361	1.2359	6
1,3,10	1.0596	1.0596	5	1, 1, 15	} 1.2135	1.2139	} 4
446	1.0370	1.0370	2	3, 0, 14		1.2138	
271	1.0263	1.0263	2	4, 1, 12	1.1986	1.1986	2
722	1.0150	1.0150	4	528	1.1814	1.1816	1
084	0.9936	0.9934	4	445	1.1711	1.1711	3
274	.9734	.9733	3	446	1.1468	1.1468	3
900	} .9368	.9369	} 6	3,3,12	1.1337	1.1335	5
372		.9368		2,2,15	1.1163	1.1166	3
538	.9357	.9357	7	3,1,15	} 1.1069	1.1071	} 2
3,0,12	.9343	.9342	11	3,2,14		1.1070	
820	.9200	.9200	3	5,2,10	1.1054	1.1055	3
268	.9188	.9189	4	715	1.0830	1.0830	3
651	.8815	.8815	3	630	1.0758	1.0758	4
740	.8745	.8744	3	716	1.0635	1.0637	3
4,1,12	.8722	.8722	4	6,0,12	1.0531	1.0530	2
808	.8597	.8597	7	4,1,15	} 1.0390	1.0394	} 3
654	.8473	.8472	6	3,3,14		1.0394	
3,3,12	.8455	.8455	8				
915	.8285	.8285	2				
384	.8227	.8227	5				
660	.8113	.8114	2				
6,0,12	.8096	.8096	6				
924	.8001	.8001	6				

^a *d*—Interplanar spacing, *I*/*I*₀—relative intensity.

^b X-ray pattern obtained from specimen heat treated at 1400 °C for 2 h. Indexing based on hexagonal cell with *a* = 9.736 and *c* = 11.886 Å.

^c X-ray pattern obtained from specimen heat treated at 900 °C for 66 h. Indexing based on hexagonal cell with *a* = 9.860 and *c* = 18.786 Å; Low 4SrO · IrO₂ is probably metastable.

It has been reported that 4SrO · PtO₂ hydrolyzes readily on contact with water [13]. This study did not detect any hydrolysis of the 4:1 Ir compound when in contact with water at temperature up to 140 °C. However, the x-ray powder pattern of a specimen having 4:1 composition heated at 1440 °C and quenched in water indicated only the 2:1 compound and an unidentified phase (probably a hydrate). A similar experiment utilizing liquid nitrogen instead of water showed only the 4:1 compound.

Randall, Katz, and Ward [14] previously have reported the existence of a 2SrO · IrO₂ compound having the body-centered tetragonal, K₂NiF₄ type-structure with *a* = 3.89 Å and *c* = 12.92 Å. The cell dimensions for the 2:1 compound in this study are in accord. The 2:1 compound is stable in air at atmospheric pressure up to 1445 °C, the dissociation temperature. The dissociation products when heated at 1100 °C reform the 2:1 compound indicating that it is a stable phase.

An atmospheric pressure form of SrO · IrO₂ (1:1) was reported by Longo and Kafalas [15], who indexed its x-ray pattern on the basis of a unit cell with monoclinic symmetry and the following cell dimensions: *a* = 5.60 Å, *b* = 9.62 Å, *c* = 14.17 Å, and β = 93°16'.

The x-ray diffraction data obtained in the present study indicates good agreement with the cell dimensions reported. The 1:1 compound is stable in air below 1205 °C, the dissociation temperature.

b. Metastable Phases

The phase listed as low 4SrO · IrO₂ (fig. 1) formed readily in air at temperatures of 800 to 1000 °C and was detected at several compositions rich in SrO. Various experiments failed to produce a completely single phase specimen and residual amounts of other phases always persisted. The composition of the compound considered most likely is 4:1 since this mixture always produced the greatest quantity of the phase. In all probability this phase is metastable and forms only on heating. Prolonged heat treatments of the stable 4:1 compound up to 8 days at 950 °C, failed to reform the low 4:1 compound. Indexing of the x-ray pattern of the phase was accomplished by a trial and error method after a literature search did not reveal any compounds structurally similar to the low 4SrO · IrO₂. The x-ray powder pattern is given in table 2. It was indexed on the basis of a hexagonal cell with $a=9.860$ Å and $c=18.786$ Å. The low 4:1 compound metastably decomposes at 1005 °C in air forming the 4:1 and 2:1 compounds. It is somewhat unusual that the metastable low 4:1 decomposes to the 4:1 compound which itself is metastable at 1005 °C.

The 3SrO · 2IrO₂ (3:2) compound forms (probably metastable) in combination with other phases in air at atmospheric pressure between 1000 and 1200 °C. The phase also occurs as a dissociation product when a mixture SrO:2IrO₂ is heated at 1300 °C. Longo and Kafalas [15] have reported previously the existence of 3SrO · 2IrO₂, as a high pressure phase (synthesized at 10 kbar (1.0×10^9 N/m²) 1000 °C) with perovskite-related structure and a body-centered tetragonal unit cell with $a=3.90$ Å and $c=20.90$ Å. This phase is apparently similar to 3SrO · 2TiO₂, the structure of which has been proposed by Ruddlesden and Popper [16, 17]. The values obtained in the present study are in good agreement with those reported by Longo and Kafalas [15]. Several attempts to reform the 3:2 compound from the dissociation products were unsuccessful, indicating perhaps it is a metastable phase in air.

The x SrO · IrO₂ ($x > 2$) compound forms (probably metastable) in air over a wide range of compositions and always in combination with other phases. The specific composition of the x SrO · IrO₂ ($x > 2$) compound is unknown; however mixtures richer in SrO than the 2:1 molar ratio yielded the greatest quantity of the phase. Its x-ray diffraction pattern, given in table 3, was indexed on the basis of a hexagonal cell with $a=10.307$ Å and $c=12.634$ Å. Trace amounts of the x SrO · IrO₂ ($x > 2$) compound form as one of the decomposition products when the 4:1 compound is given prolonged heat treatment at 1000 °C.

Table 3 gives the x-ray diffraction pattern for the y SrO · IrO₂ ($4 > y > 2$) compound indexed on the basis of a hexagonal cell with $a=9.805$ Å and $c=23.699$ Å. It exists at 900 to 1000 °C at various compositions and

TABLE 3. X-ray diffraction powder data for the x SrO · IrO₂ ($x > 2$) and y SrO · IrO₂ ($4 > y > 2$) phases (CuK α radiation)^a

x SrO · IrO ₂ ($x > 2$) ^b				y SrO · IrO ₂ ($4 > y > 2$) ^c			
$d(\text{Å})$				$d(\text{Å})$			
hkl	obs	calc	I/I_0	hkl	obs	calc	I/I_0
111	4.774	4.772	46	100	8.51	8.49	19
003	4.211	4.211	22	102	6.90	6.90	18
201		4.208		004	5.93	5.92	6
112		3.993		110	4.908	4.903	13
203	3.062	3.063	5	112	4.532	4.530	33
212	2.975	2.976	76	200	4.251	4.246	7
300		2.975		202	3.999	3.997	3
301		2.896		006	3.952	3.950	4
221	2.524	2.525	16	114	3.781	3.777	5
303	2.429	2.430	12	210	3.211	3.210	12
311		2.430		116	3.076	3.076	69
214	2.307	2.306	2	206	2.893	2.892	3
401	2.197	2.198	3	300	2.831	2.830	100
304	2.167	2.166	2	108	2.798	2.797	6
402	2.103	2.104	27	304	2.553	2.554	7
				118	2.536	2.536	28
				216	2.490	2.491	6
				305	2.429	2.430	7
				208		2.429	
				222		2.400	3
				310	2.356	2.355	5
				312	2.310	2.310	4
				225	2.178	2.177	13
				218		2.177	
				1,1,10		2.134	5
				226	2.082	2.083	30
				308	2.046	2.046	4
				1,1,11	1.973	1.972	3
				320	1.948	1.948	5
				228	1.888	1.889	12
				324	1.851	1.851	4
				318	1.843	1.843	4
				412	1.831	1.831	10
				3,0,10	1.817	1.817	5
				326	1.747	1.747	3
				2,2,10	1.703	1.704	3
				416	1.677	1.678	13
				330	1.634	1.634	9
				504	1.633	1.633	13
				332	1.619	1.619	6
				418	1.570	1.571	10
				2,2,12	1.537	1.538	4
				510	1.524	1.525	3
				600	1.415	1.415	8
				522	1.3507	1.3509	4
				526	1.2857	1.2857	5
				528	1.2354	1.2358	4

^a d —Interplanar spacing, I/I_0 —relative intensity.

^b X-ray pattern obtained from 3SrO:IrO₂ mixture heat treated at 900 °C for 17 h. Indexing based on hexagonal cell with $a=10.307$ and $c=12.634$ Å; x SrO · IrO₂ ($x > 2$) is probably metastable.

^c X-ray pattern obtained from 3SrO:IrO₂ mixture heat treated at 1000 °C for 2 h. Indexing based on hexagonal cell with $a=9.805$ and $c=23.699$ Å; y SrO · IrO₂ ($4 > y > 2$) is probably metastable.

always occurs in combination with other phases. Attempts to prepare single phase specimens were not successful. The specific composition of the

$y\text{SrO} \cdot \text{IrO}_2$ ($4 > y > 2$) compound is unknown, however the x-ray patterns indicate its composition is probably between the 4:1 and 2:1 molar ratios. The $y\text{SrO} \cdot \text{IrO}_2$ ($4 > y > 2$) compound forms only on heating and probably is metastable in air at atmospheric pressure.

The $z\text{SrO} \cdot \text{IrO}_2$ ($2 > z > 1$) compound formed (probably metastable) predominately at the 3:2 molar ratio between 1000 and 1100 °C. This phase, always in combination with other phases, formed only on heating. Various experiments failed to produce a single phase specimen and the specific composition of the compound is also unknown. The unindexed x-ray diffraction powder pattern for the $z\text{SrO} \cdot \text{IrO}_2$ ($2 > z > 1$) compound is given in table 4.³

The $2\text{SrO} \cdot 3\text{IrO}_2$ (2:3) compound was formed most readily and was detected during the preparation of almost every composition at 800 °C although never as single phase. Powder x-ray diffraction data for this phase is given in table 4. The pattern was indexed on the basis of a body-centered cubic cell with $a = 9.344$ Å. At 1025 °C the 2:3 compound dissociates to the 1:1 compound and Ir. Prolonged heating of the dissociation products failed to reform the 2:3 compound, indicating perhaps it is a metastable phase that forms only on heating. However, a mixture of the 1:1 compound and amorphous IrO_2 did form small amounts of the 2:3 phase, whereas crystalline IrO_2 and the 1:1 compound did not react. All experiments conducted in an effort to produce single phase specimens were unsuccessful. The composition considered most likely for the body-centered cubic phase is the 2:3 molar ratio. This mixture yielded the greatest quantity of the phase. Longo⁴ has pointed out that the $2\text{SrO} \cdot 3\text{IrO}_2$ compound has similar intensities and unit cell dimensions to $\text{La}_4\text{Re}_6\text{O}_{19}$ [18]. However, the discrepancy in oxygen content has not been explained.

c. Compound Summary

Table 5 summarizes the x-ray and stability data for the intermediate phases detected in this study and those reported in the literature for the $\text{SrO}-\text{IrO}_2$ pseudobinary system. Of the eleven intermediate phases tabulated, nine were identified in this study. Three stable and six probably metastable phases occur in air at atmospheric pressure.

Other investigators have generally used Ir metal as a starting material for the preparation of mixtures in the $\text{SrO}-\text{IrO}_2$ system. Several of the metastable phases detected in this study had a tendency to form only on heating and when utilizing amorphous IrO_2 as a starting material. For this reason others may not have detected the metastable phases.

Longo and Kafalas reported a series of compounds in the $\text{SrO}-\text{IrO}_2$ system with closely related perovskite-

TABLE 4. X-ray diffraction powder data for $z\text{SrO} \cdot \text{IrO}_2$ ($2 > z > 1$) and $2\text{SrO} \cdot 3\text{IrO}_2$ ($\text{CuK}\alpha$ Radiation)^a

$z\text{SrO} \cdot \text{IrO}_2$ ($2 > z > 1$) ^b		$2\text{SrO} \cdot 3\text{IrO}_2^c$			
$d(\text{\AA})$	I/I_0	$d(\text{\AA})$			
		hkl	obs	calc	I/I_0
7.2367	4	110	6.62	6.61	52
6.9154	6	200	4.68	4.67	37
5.6647	27	211	3.82	3.81	10
5.3326	4	220	3.307	3.303	14
^d 4.9374	19	310	2.957	2.955	100
4.6840	4	222	2.699	2.697	18
4.4734	12	321	2.498	2.497	74
3.8274	7	400	2.337	2.336	12
3.3445	6	330	2.202	2.202	7
3.2372	5	420	2.089	2.089	2
3.1486	7	422	1.906	1.907	12
^d 2.8482	100	510	1.833	1.832	44
2.8254	18	521	1.705	1.706	5
2.6859	17	530	1.602	1.602	15
2.5707	16	600	1.556	1.557	26
2.5149	3	611	1.5154	1.5157	13
2.2939	4	620	1.4771	1.4773	7
2.2435	4	541	1.4413	1.4417	4
2.1974	3	631	1.3778	1.3776	14
2.1435	4	444	1.3488	1.3486	5
2.1367	6	550	1.3213	1.3214	9
2.0882	5	640	1.2952	1.2957	2
2.0606	6	730	1.2269	1.2269	6
1.9997	6	651	1.1864	1.1866	8
1.9653	5	800	1.1679	1.1679	2
1.9517	8	741	1.1501	1.1501	1
1.9286	3	653	1.1165	1.1168	5
1.8656	7	660	1.1010	1.1011	6
1.7471	4	743	1.0862	1.0862	12
1.6695	3	910	1.0317	1.0318	3
^d 1.6466	7	761	1.0077	1.0075	4
1.6420	7	932	0.9637	0.9637	4
		941	.9438	.9438	4
		860	.9342	.9343	1
		10,2,2	.8990	.8991	3
		10,3,1	.8910	.8909	5
		961	.8602	.8601	4
		10,4,2	.8530	.8529	4
		11,1,0	.8459	.8459	5
		963	.8324	.8324	2
		970	.8194	.8195	2
		10,4,4	.8132	.8132	3
		972	.8072	.8072	4

^a d -Interplanar spacing, I/I_0 relative intensity.

^b X-ray pattern obtained from specimen $3\text{SrO} : 2\text{IrO}_2$ heat treated at 1000 °C for 2 h; $z\text{SrO} \cdot \text{IrO}_2$ ($2 > z > 1$) is probably metastable.

^c X-ray pattern obtained from specimen heat treated at 900 °C for 17 h. Indexing based on body-centered cubic cell with $a = 9.344$ Å; $2\text{SrO} \cdot 3\text{IrO}_2$ is probably metastable.

^d These d -spacings in decreasing order may correspond to the hexagonal indices (110), (300), (330) based on $a = 9.87$ Å.

³ The x-ray diffraction powder patterns for all the low temperature metastable hexagonal phases appear to be quite similar. An attempt was made to index the x-ray pattern for $z\text{SrO} \cdot \text{IrO}_2$ ($2 > z > 1$) based on a hexagonal cell with $a = 9.87$ Å, assuming the d values indicated in table 4 correspond to the (110), (300), and (330) reflections. Although the c value necessary to account for all the data was unreasonable large, it seems possible the phase also has hexagonal symmetry.

⁴ Personal communication.

TABLE 5. *Compounds in the SrO-IrO₂ system*

Composition	Symmetry	Unit cell (Å)				Stability data	References
		<i>a</i>	<i>b</i>	<i>c</i>	β		
4SrO · IrO ₂	hexagonal (rhombohedral)	9.736		11.886		Stable in air at atmospheric pressure between 1220 and 1540 °C (dissociation temperature).	Present work.
Low 4SrO · IrO ₂	hexagonal	9.860		18.786		Forms (probably metastable) in air at atmospheric pressure up to 1005 °C (metastable phase transformation).	Present work.
<i>x</i> SrO · IrO ₂ (<i>x</i> > 2)	hexagonal	10.307		12.634		Forms (probably metastable) in combination with other phases in air at atmospheric pressure at 900 °C.	Present work.
<i>y</i> SrO · IrO ₂ (4 > <i>y</i> > 2)	hexagonal	9.805		23.699		Forms (probably metastable) in combination with other phases in air at atmospheric pressure at 800 °C.	Present work.
2SrO · IrO ₂	tetragonal ^a (body-centered)					Stable in air at atmospheric pressure up to 1445 °C (dissociation temperature).	Present work.
		3.89		12.92			Randall, Katz, and Ward [14].
<i>z</i> SrO · IrO ₂ (2 > <i>z</i> > 1)	unindexed					Forms (probably metastable) in combination with other phases in air at atmospheric pressure at 1000 °C.	Present work.
3SrO · 2IrO ₂	tetragonal ^a (body-centered)	3.90		20.90		Synthesized at 10 kbar (1.0 × 10 ⁹ N/m ²) 1000 °C. Forms (probably metastable) in combination with other phases in air at atmospheric pressure at 1000 °C. Also occurs as a dissociation product when a mixture SrO:2IrO ₂ is heated at 1300 °C.	Longo and Kafalas [15]. Present work.
4SrO · 3IrO ₂	tetragonal (body-centered)	3.93		28.4		Synthesized at 35 kbar (3.5 × 10 ⁹ N/m ²) 1000 °C. Phase not detected in air at atmospheric pressure.	Longo and Kafalas [15]. Present work.
SrO · IrO ₂	monoclinic ^a					Stable in air at atmospheric pressure up to 1205° (dissociation temperature).	Present work.
		5.60	9.62	14.17	93°16'		Longo and Kafalas [15].
High SrO · IrO ₂	orthorhombic	5.58	5.60	7.89		Synthesized at 45 kbar (4.5 × 10 ⁹ N/m ²) 1000 °C. Phase not detected in air at atmospheric pressure.	Longo and Kafalas [15]. Present work.
2SrO · 3IrO ₂	cubic (body-centered)	9.344				Forms (probably metastable) in air at atmospheric pressure up to 1025 °C (dissociation temperature).	Present work.

^a Cell dimensions obtained in the present study are in good agreement.

type structure [15]. The structural series extends between the SrO · IrO₂ and 2SrO · IrO₂ compounds and includes in addition to the end members, the 4SrO · 3IrO₂ and 3SrO · 2IrO₂ phases. Of these perovskite-related compounds the 1:1 and 4:3 apparently can be formed

only at high pressures and thus were not detected in the present study.

With the exception of the 2:3 compound, all the low temperature metastable phases detected here have hexagonal or pseudohexagonal symmetry with a similar

a -dimension. It is possible that some undetermined structural relationship exists between these phases which could include the 2:3 compound as a member of the series. If this is true, the cubic symmetry designated for the 2:3 compound would represent a pseudocell and the true symmetry may be hexagonal.

4. References

- [1] Schneider, S. J., Waring, J. L., and Tressler, R. E., J. Res. Nat. Bur. Stand. (U.S.), **69A** (Phys. and Chem.), No. 3, 245-254 (May-June 1965).
- [2] McDaniel, C. L. and Schneider, S. J., J. Res. Nat. Bur. Stand. (U.S.), **71A** (Phys. and Chem.), No. 2, 119-123 (Mar.-Apr. 1967).
- [3] McDaniel, C. L. and Schneider, S. J., J. Res. Nat. Bur. Stand. (U.S.), **72A** (Phys. and Chem.), No. 1, 27-37 (Jan.-Feb. 1968).
- [4] Barber, C. R., Metrologia **5** [2], 35-44 (1969).
- [5] Swanson, H. E., Gilfrich, N. T., and Ugrinic, G. M., Nat. Bur. Stand. (U.S.), Circ. 539, 68 pages (1955).
- [6] Schumacher, E. E., J. Am. Chem. Soc. **48**, 396-405 (1926).
- [7] Swanson, H. E., Fuyat, R. K., and Ugrinic, G. M., Nat. Bur. Stand. (U.S.), Circ. 539, 10 pages (1955).
- [8] Swanson, H. E., Morris, M. C., and Evans, E. H., Nat. Bur. Stand. (U.S.), Monogr. 25, Sect. 4, 85 pages (1965).
- [9] Muan, A., Am. J. Sci. **256**, 171-207 (1958).
- [10] Negas, T. and Roth, R. S., J. Res. Nat. Bur. Stand. (U.S.), **73A** (Phys. and Chem.), No. 4, 431-442 (Nov.-Dec. 1969).
- [11] Schafer, H. and Heitland, H. J., Z. Anorg. Allgem. Chem. **304**, 249 (1960).
- [12] Cordfunke, E. H. P. and Meyer, G., Rec. Trav. Chim. **81**, 495-504 (1962).
- [13] Randall, J. J. and Katz, L., Acta Cryst. **12**, 519-21 (1959).
- [14] Randall, J. J., Katz, L., and Ward, R., J. Am. Chem. Soc. **79**, 266-7 (1957).
- [15] Longo, J. M., Kafalas, J. A., and Arnott, R. J., J. Solid State Chem. **3**, (1971).
- [16] Ruddlesden, S. N. and Popper, P., Acta Cryst. **10**, 538 (1957).
- [17] Ruddlesden, S. N. and Popper, P., Acta Cryst. **11**, 54 (1958).
- [18] Longo, J. M. and Sleight, A. W., Inorg. Chem. **7**, 108-111 (1968).

(Paper 75A3-662)